

## Flooring adhesives

The present invention relates to an aqueous composition  
5 comprising a mixture of

from 10 to 50% by weight of a polymer A) having a gel content of  
less than 40% by weight and a number-  
average molecular weight  $M_n$  of the  
10 soluble fractions of less than 30,000  
and

from 50 to 90% by weight of a filler B), the amounts by weight  
being based on the weight sum of the  
15 polymer A) and of the filler B).

The invention additionally relates to the use of this aqueous  
composition as an adhesive for floor coverings.

20 Adhesives are generally required to display good adhesion - in  
other words, to stick well to the substrate - and good cohesion -  
in other words, to hold together well within the adhesive layer.  
Adhesives for floor coverings are subject to particular  
requirements. Here, there is a desire in particular for good wet  
25 bonding capacity. A good wet bonding capacity means that after a  
carpet, for example, has been laid on the substrate which is  
coated with the aqueous dispersion the carpet can initially still  
be aligned and its position corrected, but that soon after a  
slipproof bond develops whose strength increases as drying  
30 progresses.

A good dry bonding capacity means that even after a prolonged  
period of ventilation a carpet, after having been laid on the  
substrate, which is then dry, gives a firm, slipproof bond.

35 A further desire is to dispense with volatile organic  
constituents, such as solvents or plasticizers, in order to avoid  
subsequent exposure to corresponding emissions.

40 A low binder content is also desirable. When tackifiers are  
added, the level of properties should remain as good as possible  
- especially the cohesion.

Flooring adhesives are already known from EP-A-490191 and  
45 WO 95/21884.

It is an object of the present invention to provide flooring adhesives having improved performance properties, in particular a good wet bonding capacity.

- 5 A further object is to keep the binder content in the flooring adhesives as low as possible on cost grounds. Where the addition of tackifiers (tackifying resins) is desired, this should be possible without adverse effect on, for example, wet and dry bonding capacity.

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We have found that these objects are achieved by the aqueous composition described above and by its use as a flooring adhesive.

- 15 The aqueous composition comprises preferably

from 10 to 45% by weight, with particular preference from 15 to 40% by weight, of the polymer A) defined at the outset, and

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from 55 to 90% by weight, with particular preference from 60 to 85% by weight, of a filler B).

The percentages by weight are based in each case on the weight

- 25 sum of A) and B).

The polymer A) is preferably a free-radically polymerized polymer of ethylenically unsaturated monomers.

- 30 The polymer preferably comprises principal monomers selected from C<sub>1</sub>-C<sub>20</sub>-alkyl (meth)acrylates, vinyl esters of carboxylic acids having up to 20 carbons, vinylaromatic compounds having up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl halides, nonaromatic hydrocarbons having at least 2 conjugated  
35 double bonds, or mixtures of these monomers.

The abovementioned monomers and mixtures thereof are preferably present in the polymer to an extent of from 60 to 100% by weight, preferably from 80 to 100% by weight and, with particular

- 40 preference, from 90 to 99.8% by weight, based on the polymer.

Mention may be made specifically, for example, of C<sub>1</sub>-C<sub>10</sub>-alkyl (meth)acrylates, such as methyl methacrylate, methyl acrylate, n-butyl acrylate, ethyl acrylate and 2-ethylhexyl acrylate.

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Mixtures of the (meth)acrylic alkyl esters are also particularly suitable.

Examples of vinyl esters of carboxylic acids having 1 to 5 20 carbon atoms are vinyl laurate, vinyl stearate, vinyl propionate, Versatic acid vinyl ester and vinyl acetate.

Suitable vinylaromatic compounds are vinyltoluene,  $\alpha$ - and p-methylstyrene,  $\alpha$ -butylstyrene, 4-n-butylstyrene, 4-n-decyl- 10 styrene and, preferably, styrene. Examples of nitriles are acrylonitrile and methacrylonitrile.

The vinyl halides are ethylenically unsaturated compounds substituted by chlorine, fluorine or bromine, preferably vinyl 15 chloride and vinylidene chloride.

As nonaromatic hydrocarbons having 2 to 8 carbon atoms and at least two olefinic double bonds there may be mentioned butadiene, isoprene and chloroprene.

20 Particular preference is given to (meth)acrylic esters and mixtures thereof.

Further monomers, which may be present in the polymer to the 25 extent, for example, of from 0 to 40% by weight, preferably from 0 to 20% by weight and, with particular preference, from 0.2 to 10% by weight, are, in particular,  $C_1$ - $C_{10}$ -hydroxyalkyl (meth)acrylates, (meth)acrylamide and its N- $C_1$ - $C_4$ -alkyl-substituted derivatives, ethylenically unsaturated carboxylic 30 acids, dicarboxylic acids, their monoesters and anhydrides, examples being (meth)acrylic acid, maleic acid, fumaric acid, maleic anhydride, maleic and fumaric monoesters and itaconic acid. Very particular preference is given to a content of from 0.2 to 5% by weight of an ethylenically unsaturated carboxylic 35 acid.

The glass transition temperature of the polymer is preferably from  $-50$  to  $+20^\circ\text{C}$ , in particular from  $-35^\circ\text{C}$  to  $+20^\circ\text{C}$ , with particular preference from  $-30^\circ\text{C}$  to  $0^\circ\text{C}$  and, with very particular 40 preference, from  $-28^\circ\text{C}$  to  $-5^\circ\text{C}$ .

The glass transition temperature of the polymer can be determined by customary methods such as differential thermoanalysis or differential scanning calorimetry (see e.g. ASTM 3418/82, 45 midpoint temperature).

The gel content of the polymer A) is below 40% by weight, preferably below 30% by weight and, with particular preference, below 20% by weight, based on the polymer A). The gel content should preferably be more than 5% by weight.

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The gel content is the content of insoluble constituents. It is defined and determined by the following method: the dispersion is dried at 21°C to give a film approximately 1 mm thick. One gram of the polymer film is added to 100 ml of tetrahydrofuran and is  
10 allowed to stand at 21°C for a week. Thereafter, the resulting solution or mixture is filtered with the aid of a cloth filter (mesh size 125  $\mu$ m). The residue (swollen film) is dried at 21°C for 2 days in a vacuum drying cabinet and then weighed. The gel content is the mass of the weighed residue, divided by the mass  
15 of the polymer film employed.

✓ The tetrahydrofuran-soluble fractions of the polymer are, correspondingly, from 60 to 100% by weight, preferably from 70 to 100% by weight, with particular preference from 80 to 100% by  
20 weight and, in particular, up to 95% by weight, based on the polymer.

The number-average molecular weight  $M_n$  of these soluble fractions is preferably less than 20,000, preferably less than 15,000, and  
25 the weight-average molecular weight  $M_w$  is preferably greater than 250,000 (as determined by gel permeation chromatography with polystyrene as standard on a polymer solution in tetrahydrofuran following sedimentation of the insoluble constituents).

30 Generally, however,  $M_n$  is not less than 5000 g/mol and  $M_w$  is not more than 800,000 g/mol.

The polymer is prepared by free-radical polymerization. Suitable methods of polymerization, such as bulk, solution, suspension or  
35 emulsion polymerization, are known to the skilled worker.

The copolymer is preferably prepared by solution polymerization with subsequent dispersion in water or, with particular preference, by emulsion polymerization, to give aqueous copolymer  
40 dispersions.

An emulsion polymerization can be conducted batchwise, with or without the use of seed latices, with all or some constituents of the reaction mixture being included in the initial charge, or,  
45 preferably, with some being included in the initial charge and the remainder of all or some constituents of the reaction mixture being metered in subsequently, or else in accordance with the

metering technique without an initial charge.

In emulsion polymerization, the monomers can as usual be polymerized in the presence of a water-soluble initiator and an emulsifier at preferably from 30 to 95°C.

Examples of suitable initiators are sodium, potassium and ammonium persulfate, tert-butyl hydroperoxides, water-soluble azo compounds, or redox initiators, such as  $H_2O_2$ /ascorbic acid.

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Examples of the emulsifiers used are alkali metal salts of relatively long-chain fatty acids, alkyl sulfates, alkyl-sulfonates, alkylated arylsulfonates or alkylated biphenyl ether sulfonates. Further suitable emulsifiers are reaction products of alkylene oxides, especially ethylene or propylene oxide, with fatty alcohols, fatty acids or phenol, or else with alkylphenols.

In the case of aqueous secondary dispersions the copolymer is first of all prepared by solution polymerization in an organic solvent and then is dispersed in water without using an emulsifier or dispersing auxiliary but with addition of salt-forming agents, for example ammonia for carboxyl-containing copolymers. The organic solvent can be removed by distillation. The preparation of aqueous secondary dispersions is known to the skilled worker and is described, for example, in DE-A-37 20 860.

In the course of polymerization it is possible to employ regulators to adjust the molecular weight. Suitable examples are SH-containing compounds, such as mercaptoethanol, mercapto-propanol, thiophenol, thioglycerol, ethyl thioglycolate, methyl thioglycolate and tert-dodecyl mercaptan.

The solids content of the resulting polymer dispersions is preferably from 40 to 80% and, with particular preference, from 45 to 75% by weight. High polymer solids contents can be established, for example, by techniques which are described in the German Patent Application P 4 307 683.1 or in EP 37 923.

In addition to the polymer the aqueous composition comprises at least the filler B). Examples of suitable such fillers are finely ground or precipitated chalks having an average particle diameter of in general from 2 to 50  $\mu m$ , and/or quartz flour having a customary average particle diameter of from 3 to 50  $\mu m$ .

The composition may also include wetting agents or dispersants for the fillers, for example; thickeners, and also, for example,

further customary additives, such as defoamers and preservatives.

Wetting or dispersing agents can be present in the aqueous composition in amounts, for example, of from 0 to 5% by weight, 5 thickeners in amounts from 0 to 10% by weight, preservatives in amounts from 0 to 1% by weight and defoamers in amounts from 0 to 5% by weight. These amounts by weight relate to the sum of all constituents of the aqueous composition with the exception of the water.

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The composition is preferably essentially free and with particular preference totally free from organic solvents and plasticizers such as butyl acetate, toluene or phthalates, for example. It therefore comprises organic compounds having a 15 boiling point below 300°C at atmospheric pressure (1 bar) in amounts of less than preferably 0.5% by weight, with particular preference less than 0.1% by weight and, with very particular preference, less than 0.05% by weight, and in particular less than 0.01% by weight. It is particularly preferred for the 20 composition of the invention or the flooring adhesive of the invention to meet the requirements of freedom from emissions as defined by GEV [German Association for Controlled Emission Installation Materials].

25 The emissions are determined by a chamber test method. The flooring adhesive or composition of the invention is applied at a rate of 300 g/m<sup>2</sup> to a glass plate whose size depends on the volume of the chamber. The chamber is loaded with 0.4 m<sup>2</sup> of the coated glass plate per m<sup>3</sup> of chamber volume. The emission conditions in 30 the stainless steel testing chamber (volume at least 125 liters) are 23°C, 50% relative atmospheric humidity and an hourly air-change regime which brings about total exchange of the air every 2 hours. The long-term emissions are determined after 10 days. For this purpose, a defined volume of the airstream is 35 passed over adsorbents. Following desorption, the emitted substances are determined by gas (GC-MS coupling) or liquid chromatography. The long-term emissions are determined in µg/m<sup>3</sup>, using toluene as standard substance. Emitted substances whose chamber concentration is greater than 20 µg/m<sup>3</sup> are identified, and 40 with the pure substance identified and calibrated [sic]. Emitted substances whose chamber concentration is less than 20 µg/m<sup>3</sup> are not identified individually. In such cases, calibration take place with toluene.

45 The values for all the substances are added up.

In the case of the composition of the invention, the emission value for the sum of all organic compounds is not more than preferably 1500  $\mu\text{g}/\text{m}^3$  and in particular not more than 500  $\mu\text{g}/\text{m}^3$ .

- 5 The composition can comprise tackifying resins (tackifiers), such as rosins or modified rosins, based, for example, on hydrogenated abietic acid or abietic esters.

The content of tackifiers can preferably be from 1 to 40 parts by  
10 weight, based on 100 parts by weight of the sum of polymer A) and filler B).

The aqueous composition can be prepared in a simple manner by adding the fillers and any further additives with stirring to the  
15 aqueous polymer dispersion resulting from the emulsion polymerization.

The water content of the finished formulation is generally from 7 to 50, in particular from 10 to 30% by weight, based on the  
20 overall aqueous formulation.

The aqueous composition is particularly suitable as an adhesive for bonding substrates made from plastic, wood, metal and textiles formed from woven and/or nonwoven fibers.

- 25 The aqueous formulation is particularly suitable as a flooring adhesive for carpets or other floor coverings made, for example, from PVC (in configurations as multilayer coverings or homogeneous coverings), foam coverings with a textile backing  
30 (e.g. jute), polyester nonwoven, rubber coverings, textile coverings with, for example, various backings (for instance, polyurethane foam, styrene-butadiene foam, a textile secondary backing), needlefelt floor coverings, polyolefin coverings or linoleum coverings, on substrates such as wood, screeding,  
35 concrete, ceramic tiles, metal substrates or the like.

The adhesive can be applied to the substrate using, for example, a toothed applicator. After customary venting, the floor covering is installed. In terms of processing, the adhesive of the  
40 invention resembles the solvent-containing synthetic-resin adhesives and the conventional single-side dispersion adhesives. In terms of ease of application, the novel adhesive resembles solvent-containing adhesives. The adhesive composition of the invention features a good level of performance properties such as  
45 peel strength, shear strength, wet bonding capacity and dry gripping capacity. The composition of the invention achieves this good level of properties with a markedly reduced content of

binder, i.e. of polymer A). Even following the addition of tackifiers in order, for example, to increase the tackiness, the wet bonding strength remains at a high level.

- 5 The parts and percentages indicated in the examples which follow are by weight unless specified otherwise.

### Examples

#### 10 I. Dispersions

The table below lists a number of commercial products which are recommended for flooring adhesives, for comparison. In its monomer composition, Acronal DS corresponds to Acronal 378 and therefore has the same glass transition temperature ( $T_g$ ). The content of regulator was varied in order to obtain the desired molecular weight.

Table 1: Physical data of the dispersions

20	Dispersion	SC	$M_n$	$M_w$	$M_w/M_n$	Gel content % by weight	$T_g/^\circ\text{C}$
	Acronal A200 for comparison	70%	26,000	416,00 [sic]	16	54%	-47
25	Acronal A323 for comparison	55%	5800	753,000	130	70%	-22
	Acronal 378 for comparison	62%	22,000	437,000	20	68%	-22
	Acronal DS	62%	11,900	354,000	30	15%	-22

- 30 SC: Solids content  
 $T_g$ : Glass transition temperature

#### II. Flooring adhesives

- 35 The dispersions were mixed with filler and with further additives.

Table 2 sets out the co-components and their proportions by weight.

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Table 2

	Experiment	1	2	3	4
5	Acronal A 200	24.4			
	Acronal A 323		31.0		
	Acronal DS 378			27.5	
	Acronal DS				27.5
10	2% strength Latekoll D solution <sup>1)</sup>	14.6	8.0	11.5	11.5
	Agitan 281 <sup>2)</sup>	0.2	0.2	0.2	0.2
	Lutensol AO 109 <sup>3)</sup>	0.5	0.5	0.5	0.5
	Lumiten N-OG <sup>4)</sup>	0.5	0.5	0.5	0.5
15	Pigmentverteiler NL <sup>5)</sup>	0.5	0.5	0.5	0.5
	Calgon N 30 <sup>6)</sup>	1.0	1.0	1.0	1.0
	Sodium gluconate <sup>7)</sup>	1.5	1.5	1.5	1.5
	Burez LE 3004 <sup>8)</sup>	11.0	11.0	11.0	11.0
	Ulmer Weiss XM <sup>9)</sup>	45.8	45.8	45.8	45.8

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The amount of the polymer dispersion was determined so as to give in each case 17 parts by weight of polymer (solids).

The amount of thickener (Latekoll) was determined so that the  
25 viscosity was equal.

- 1): Thickener
- 2): Defoamer
- 3): Emulsifier
- 30 4): Emulsifier
- 5): Dispersant for pigment
- 6): Dispersant for pigment
- 7): -
- 8): Tackifier (resin based on the triethylene glycol ester of  
35 abietic acid)
- 9): Filler

### III. Performance testing

40 - Wet bonding capacity (WBC):

The adhesive is applied with a DIN blade to a cement fiberboard panel (e.g. Eternit® 2000; 20 x 50 cm) in the direction of takeoff. The amount applied is about 350 - 400 g/m<sup>2</sup>. Needlefelt floor covering strips are placed in the bed of adhesive following a venting period of 10 minutes and are pressed on with a 2.5 kg roller by rolling backward and

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forward 3 times. At the stated intervals of time, the strips are pulled off with a takeoff apparatus, during which the increase in the peel resistance is determined in N 5 cm.

5 The results are set out in Table 3.

- Peel strength: determined in accordance with DIN 53269

Table 3

10		Peel values N/mm		WBC N/5 cm			
		10 min	30 min	10 min	15 min	20 min	30 min
15	1 (for comparison)	0.34	0.24	4	7	9	8
	2 (for comparison)	0.91	0.07	2	5	11	22
	3 (for comparison)	1.38	0.18	4	10	19	34
non	4	1.22	0.24	12	26	44	49

gel content  
outside  
pc

invention

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